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(54) QUARTZ GLASS OPTICAL MEMBER, ITS PRODUCTION, AND PROJECTION EXPOSURE DEVICE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a quarty glass optical member used for an optical system in a prescribed wavelength region, improving the transmittance of the optical system of UV light, vacuum UV light or the same wavelength region lasers by specifying the concentration of Na contained in quartz glass.

SOLUTION: In the optical member sued in an optical system having a wavelength region of ≤ 250nm (e.g. ArF excimer laser stepper), the concentration of Na contained in the quartz glass is controlled to ≤20ppb. The concentrations of Na and Al are controlled to ≤50ppb and 5-100ppb, respectively. The concentrations of the elements of transition metals and alkali (alkaline earth) metals are controlled to ≤20ppb, respectively. The method for producing the quartz glass for the optical members comprises hydrolyzing a highly pure Si compound in an oxygen-hydrogen flame blown out from a burner in a synthesis oven and subsequently depositing the formed soot on a target to form the glass. Therein, the distance between a soot-reached position on the target and the wall of the synthesis over is controlled to ≥250nm. Thereby, the contamination of impurities from the synthesis oven can be prevented.

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CLAIMS

[Claim(s)]
[Claim 1] the quartz-glass optics characterized by the concentration of Na contained in quartz glass being 20 or less ppb in the quartz-glass optical member used for the optical system of a wavelength field 250nm or less -- a member
[Claim 2] the quartz-glass optics characterized by for the concentration of Na contained in quartz glass being 50 or less ppb in the quartz-glass optical member used for the optical system of a wavelength field 250nm or less, and the concentration of aluminum being 5 - 100ppb -- a member
[Claim 3] the quartz glass characterized by the concentration of each element of the transition metals contained in quartz glass, alkali metal, and alkaline earth metal being 20 or less ppb of each in a quartz-glass optical member according to claim 1 or 2 -- a member
[Claim 4] the quartz-glass optics to which the mol concentration ratio of Na and aluminum contained in quartz glass is characterized by being [Na] / [aluminum] <=1 in the quartz-glass optical member used for the optical system of a wavelength field 250nm or less -- a member
[Claim 5] The manufacture method of the quartz glass characterized by setting the distance of the position where the aforementioned particle reached the target, and a synthetic furnace wall as 250mm or more in the manufacture method of the quartz glass which understands an added water part in the oxygen hydrogen flame which blows off the silicon compound of a high grade from a burner in a synthetic furnace, forms a quartz-glass particle, deposits on a target, and is vitrified.
[Claim 6] The manufacture method of the quartz glass characterized by being the refractories with which the refractories which understand an added water part in the oxygen hydrogen flame which blows off the silicon compound of a high grade from a burner in a synthetic furnace, form a quartz-glass particle, and form the furnace wall of a synthetic furnace in the manufacture method of the quartz glass which deposits on a target and is vitrified make an alumina a principal component.
[Claim 7] the lighting optical system which is equipment which carries out projection exposure of the pattern image of a mask on a substrate using a projection optical system, and illuminates a mask by making light of a wavelength field 250nm or less into exposure light, and the projection optical system which forms the pattern image of the aforementioned mask on a substrate including a quartz-glass optical member according to claim 1 to 4 -- a shell -- a projection aligner
[Claim 8] the lighting optical system which is equipment which carries out projection exposure of the pattern image of a mask on a substrate using a projection optical system, and illuminates a mask including a quartz-glass optical member according to claim 1 to 4 by making light of a wavelength field 250nm or less into exposure light, and the projection optical system which forms the pattern image of the aforementioned mask on a substrate -- a shell -- a projection aligner

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[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the optical lithography equipment which used the quartz-glass optical member used as optical elements, such as lens members, such as optical system for lighting which used laser of ultraviolet [, such as for example, excimer laser lithography equipment, a photon assisted CVD system, and laser-beam-machining equipment, / 250nm or less], vacuum ultraviolet radiation, or this wavelength field as the light source, or optical system for image formation, a fiber, window part material, a mirror, an etalon, and prism, and its quartz-glass optical member for some or all of the optical system.
[0002]
[Description of the Prior Art] Conventionally, the reduction projection type aligner called stepper in the optical lithography technology which exposes and imprints the detailed pattern of an integrated circuit on wafers, such as silicon, is used. The optical system of this stepper consists of lighting optical system which illuminates the light of the light source uniformly on the reticle on which the integrated-circuit pattern was drawn, and a projection optical system which reduces the integrated-circuit pattern of a reticle to 1 of half a sum, projects on a wafer, and is imprinted. The equipment which imprints an integrated-circuit pattern on a wafer using such a light will be named generically, and it will be called optical lithography equipment. It is necessary to make resolution of the imprint pattern on a wafer higher with high integration of LSI in recent years. Since the resolution of an imprint pattern is proportional to the numerical aperture of a projection optics lens system, and the inverse number of the wavelength of the light source at this time, it is possible by raising numerical aperture or shortening wavelength of the light source to obtain high resolution. However, since there is a limitation on lens manufacture in the numerical aperture of a lens, in order to raise resolution, wavelength of the light source must be shortened. For this reason, as for the light source of a stepper, short wavelength-ization is further advanced to KrF (248nm) or the ArF (193nm) excimer laser i lines (365nm) from g line (436nm). In order to manufacture VLSIs, such as DRAM which has the storage capacity of 64,256 megabits or 1 or 4 gigabits or more especially, it is necessary to set to 0.3 micrometers or less the line and space which are the index of the resolution of a stepper. At this time, ultraviolet [, such as an excimer laser / 250nm or less] and vacuum ultraviolet radiation must be used as the light source of a stepper.
[0003] In a short wavelength field, a light transmittance will fall rapidly, and the optical glass used from i line as a lens member of the lighting optical system of a stepper using the light source of long wavelength or a projection optical system will stop generally, penetrating light with almost all optical glass in a wavelength field 250nm or less especially rather than i line. Therefore, a material usable to the optical system of the stepper which used the excimer laser as the light source will be restricted to a part of crystal material besides quartz glass. Especially quartz glass is a material widely used for the optical system of not only an excimer laser stepper but general ultraviolet vacuum ultraviolet radiation also in it because of [in a wavelength field 250nm or less] high permeability.
[0004] However, when using quartz glass with the optical system of optical lithography equipment, in

order to expose an integrated-circuit pattern by high resolution in a big area, high quality is required very much of the quartz-glass optical member. For example, it is required that the refractive-index distribution of a member should be 10 to 6 or less ********s within very big aperture with a diameter of about 200mm. Moreover, it is important to the resolution of optical system to decrease the amount of birefringences, i.e., to decrease the internal distortion of optical faculty material, the same with raising the homogeneity of a refractive-index distribution.
[0005] Furthermore, permeability needs to be very excellent while the homogeneity about such a refractive index and distortion are quality. For example, the lens which has very many curvatures because of an aberration amendment is needed for the projection optical system of optical lithography equipment, therefore the total optical path length of the whole projection optical system may amount to 1000mm or more. In this case, in order to maintain the throughput of a projection optical system to 80% or more, the high permeability of 99.8% or more (when it converts into an internal-resorption coefficient, it is one or less [0.002cm -]) in the internal transmittance per cm of optical faculty material is needed. Furthermore, such high permeability needs to be maintained not only over the core of a member but over the whole region. For this reason, even if it only calls it quartz glass, what can be used for precise optical system like an excimer laser stepper is restricted.
[0006] Quartz glass is roughly classified into melting quartz glass and synthetic quartz glass according to a process. Melting quartz glass fuses [electrical-and-electric-equipment-] or fuses [flame-] natural crystal powder, and is obtained. Synthetic quartz glass is further classified according to the manufacture method, and is obtained by the manufacture method of vapor phase synthetic methods, such as a direct method, the soot method, and the plasma method.
[0007] First, a direct method is a method of obtaining a quartz-glass lump, by performing deposition, melting, and transparent-ization at a stretch on the target which uses the silicon compound of high grades, such as a tetrachlorosilane, for a raw material, understands a raw material an added water part by the oxygen hydrogen flame, is made to form a quartz-glass particle (soot), rotates it, and is performing reduction. Moreover, in order to make still more nearly quality the quartz-glass optical member obtained by this method, the method of performing-like secondary [further] heat treatment and acquiring desired physical properties after the primary process which compounds quartz glass, is tried. For example, it is known by performing secondary heat treatment near 2000 degree C that the homogeneity of a refractive index will improve.
[0008] Next, after the soot method uses the silicon compound of a high grade for a raw material, understands a raw material an added water part by the acid hydrogen flame, makes a soot form, makes it deposit on a target and obtains a soot lump, it is a method of carrying out the rarefaction by secondary treatment and obtaining a quartz-glass lump. Furthermore, the plasma method is a method of obtaining a quartz-glass lump, by performing deposition, melting, and the rarefaction at a stretch on the target which uses the silicon compound of a high grade for a raw material, is made to form a soot by oxidizing a raw material by the RF plasma flame of oxygen + argon mixture, rotates, and is reducing and carrying out it.
[0009]
[Problem(s) to be Solved by the Invention] Generally, the synthetic quartz glass obtained by these manufacture methods has few metal impurities as compared with melting quartz glass, and is a high grade. Therefore, it is possible to have high permeability in an ultraviolet-rays wavelength field 250nm or less, and to obtain a homogeneous quartz-glass optical member with the diameter of a large quantity, and promising ** of using synthetic quartz glass as optical system of optical lithography equipments, such as an excimer laser stepper, is carried out.
[0010] However, even if it was such synthetic quartz glass, it was very difficult to secure the permeability per 1cm of transmitted light way length of a member 99.8% or more in a wavelength field 250nm or less. Since permeability will get worse rapidly if it becomes especially a vacuum-ultraviolet field with a wavelength of 220nm or less, the amount of absorption per [which cannot be used at all as an optical member of an ArF excimer laser stepper] 1cm of optical path lengths will become several% or more.
[0011] Furthermore, like the projection optical system of optical lithography equipment, when highly

precise quartz glass was required, the homogeneity of the refractive index within very big aperture with a diameter of about 200mm and distortion needed to be quality simultaneously with good permeability, for example.
[0012]
[Means for Solving the Problem] Then, this invention persons investigated the influence of a metal impurity to the ultraviolet permeability of synthetic quartz glass first. Consequently, even if it was synthetic quartz glass whose internal transmittance is 99.9% or more per 1cm of optical path lengths in 248nm which is the wavelength of a KrF excimer laser, when the transparency property by the side of short wavelength was investigated further, permeability fell rapidly in the wavelength field 220nm or less, in 193nm which is the wavelength of an ArF excimer laser, an internal transmittance is 99% or less per 1cm of optical path lengths, and it became clear that there are some which cannot be used as an optical member.
[0013] This invention persons traced that it was in the alkali metal whose factor which governs the permeability of the field is an impurity, as a result of inquiring wholeheartedly about the cause of a rapid permeability fall of the synthetic quartz glass in a vacuum-ultraviolet field with a wavelength [such] of 220nm or less. As shown in drawing 2 , when Na concentration is set to 20 or less ppb, absorption stops occurring substantially, although especially Na has influenced the permeability of the wavelength field greatly.
[0014] Then, this invention offers the quartz-glass optical member characterized by the concentration of Na contained in quartz glass being 20 or less ppb in the quartz-glass optical member used for the optical system of a wavelength field 250nm or less. Moreover, this invention persons found out not generating absorption in a wavelength field 220nm or less substantially until they became aluminum and equivalence with mol concentration even if the content of Na increased, when aluminum was a suitable content as a still more important point.
[0015] Then, this invention offers further the quartz-glass optical member characterized by the mol concentration ratios of Na and aluminum being [Na] / [aluminum] <=1 in the quartz-glass optical member used for the optical system of a wavelength field with a wavelength of 250nm or less.
[0016]
[Embodiments of the Invention] As mentioned above, this invention found out that the cause of a rapid permeability fall of the quartz glass in an ultraviolet-rays field with a wavelength of 250nm or less, especially a vacuum-ultraviolet field with a wavelength of 220nm or less was in alkali metal, especially Na had influenced. Since air, water, a human body, etc. exist anywhere and it is easy to diffuse Na, it is matter which is very easy to mix in optical faculty material etc. as an impurity. Furthermore, if it will be in an elevated-temperature state, diffusion will further become easy to take place. for this reason -- if a quartz-glass member is heat-treated at the temperature of hundreds of degrees C or more with an electric furnace etc. -- easy -- a member -- it is spread inside and is in the cause of devitrification also with a bird clapper at the temperature of 1000 degrees C or more especially
[0017] if secondary heat treatment near 2000 degree C is performed in order that this invention persons may attain the high homogeneity required of the member of the projection optical system of for example, optical lithography equipment -- a member -- it checked experimentally that Na was easily spread inside though a high grade is made to reduce especially Na impurity how, after heat-treating the structure, for example, the heat insulator, a specimen container usually made from carbon etc. inside a heat treating furnace -- quartz glass -- a member -- it turns out inside that dozens ppb level is surely mixed
[0018] Although it was the same alkali metal, K was also understood that it hardly mixes also with the above secondary heat treatments. For example, it checked that the concentration of K could attain 50 or less ppb, and did not affect the permeability of 220nm or less with heat treatment near [above] 2000 degree C, either. This is considered to originate in the diffusion coefficient in the inside of the quartz glass of K being small as compared with Na.
[0019] Therefore, although K affects the permeability of a wavelength field 220nm or less, the influence is small as compared with Na, if it is made 50 or less ppb of concentration, does not make it generated

substantially and can carry out a permeability fall in a wavelength field 220nm or less. Based on the above point, this invention persons adopted the method of attaining homogenization of a refractive index, at the time of composition, without performing secondary heat treatment as a method of reducing the alkali-metal impurity in quartz glass, especially Na. However, even though it attains homogenization only at the time of composition, the danger of mixing in the quartz glass with which Na was done slightly is not avoided. For example, an impurity may be emitted under an elevated temperature from the refractories used as a synthetic furnace wall of quartz glass. These refractories are usually used for the surroundings of the quartz-glass ingot in a synthetic furnace as a heat insulator. then, the thing for which this invention persons maintain the distance of a quartz-glass ingot and refractories at a suitable distance -- quartz glass -- a member -- it checked that it was possible to set concentration of 20 or less ppb, and Li and K to 50 or less ppb for the concentration of Na mixed inside this invention can be attained by specifically, arranging so that the shortest may also maintain the distance from the refractories inside of a synthetic furnace to a laminating point 250mm or more. At this time, a laminating point is a place where the soot which blows off from a burner reaches an ingot head. Most soots are captured by the ingot at this laminating point.

[0020] Moreover, at the conventional synthetic furnace, the fire brick of marketing which refractories have in JIS is used. For example, they are a fireclay brick, ****** fire brick, and a high alumina brick. For example, a high alumina brick consists of about 90% of aluminum 2O3, and contains Na2O 0.5 to 1% (X-ray fluorescence analysis) as an impurity. This Na2O becomes the cause which Na distributes in quartz glass from refractories.

[0021] Then, in this invention, we made the alumina into the principal component as refractories in a synthetic furnace, and decided to use the refractories which do not contain Na2O. The refractories which consist of 99% or more of aluminum 2O3 were specifically produced, and this was used. When the quartz-glass ingot was compounded using the synthetic furnace which has these refractories, Na content in quartz glass became below limit of detection (1 or less ppb) by radiochemical analysis.

[0022] Na concentration of the synthetic quartz glass Hikari faculty material which started the configuration of desired optical faculty material, annealed and was obtained from this ingot was set to 10 or less ppb. In addition, when the refractories which make an alumina (aluminum 2O3) a principal component (99% or more) are used, also at the lowest, aluminum mixes in the quartz glass compounded more than the number ppb. Although aluminum was an impurity for quartz glass, when little aluminum coexists with Na of the same grade as this, it turns out that there is work which suppresses the produced by content of Na.

[0023] This is presumed to be based on aluminum vanishing the non-bridging oxygen produced by existence of Na in quartz glass, and making a bridge construct. That is, it is possible to lose absorption of an ultraviolet region and to acquire the outstanding ultraviolet property by making aluminum of the same grade as Na contain in the quartz glass with which Na exists in a minute amount. But since the absorption and the structure defect which are produced by aluminum itself as aluminum is a more than large quantity, for example, 100ppb, pose a problem, as for the content of aluminum, it is desirable that it is 5ppb - 100ppb.

[0024]

[Example 1]

<Composition of quartz glass> drawing 1 is the conceptual diagram showing the outline of the synthetic furnace for manufacturing synthetic quartz glass. A burner 2 turns the nose of cam to a target, and is installed in the upper part of the refractories 1 (refractories are explained later) which constitute the furnace wall of a synthetic furnace. The aperture (not shown) and exhaust pipe for observation are prepared in the furnace wall, respectively. The target 4 for ingot formation is arranged at the lower part of a synthetic furnace.

[0025] The thing of the multiplex pipe structure made from quartz glass was used for the burner. By this burner, it mixes, oxygen gas and hydrogen gas are burned, the tetrachlorosilane of a high grade (for metal impurity Fe concentration, in 99.99% or more of purity, 10 or less ppb, nickel, and Cr concentration are 2 or less ppb) is diluted with carrier gas (usually oxygen gas) as a raw material, and it

is made to blow off from the central canal of a burner by part for raw material flow rate/of 30g. When a raw material understands an added water part in the flame of a burner tip, a quartz-glass particle (soot) occurs. It rotated at the rate of 7 rotations of this in 1 minute, and rocked a 80mm travel and in a cycle of 90 seconds, and it deposited on the target board of phi 200 which is performing reduction at the speed of 4mm per hour, fused, and the ingot was compounded. The ingot upper part is covered by the flame at this time. The hydrogen gas flow rates which blow off from a burner are about 500 slm(s), and set up the ratio of an oxygen gas flow rate and a hydrogen gas flow rate with O2/H2=0.4.

[0026] Since the temperature distribution of the synthetic field of the ingot upper part become small by rotating and rocking a target board a fixed period, the homogeneity of the refractive index of the quartz glass obtained improves. Furthermore, a target board is pulled down so that the position of the synthetic field of the ingot upper part may always be maintained at the equal distance from a burner. Thus, a fixed period, there is no 3 direction stria by carrying out rotation, rocking, and reduction about a target at the time of composition, there is no birefringence accompanying a stria in it, and the homogeneity of a refractive index is acquired for 2xten to six or less quartz-glass ingot.

[0027] Moreover, at this synthetic furnace, by the shortest, the distance from the refractories which constitute a synthetic furnace wall to a synthetic field was compounded, as it was set to 300mm. A synthetic field is a place where the soot which blows off from a burner reaches the ingot upper part. Moreover, the refractories of a synthetic furnace have been arranged so that it may become an inside configuration with a 800mm[600mm by] x height of 800mm around a quartz-glass ingot, and they made into the product made from an alumina (aluminum 2O3). These refractories mixed the bubble-like alumina empty capsid with the binder of the quality of a high alumina, sintered it at 1500 degrees C for 24 hours, and removed and produced the volatile component. This consists of 99.5% or more of aluminum 2O3, and the content of Na2O is below a measurement limitation (0.03%) in an X-ray fluorescence analysis.

[0028] By this method, the quartz-glass ingot with a diameter [of 300mm] and a length of 600mm was obtained. Optical polish was given to the 2nd page which cuts down the test piece for transmissometries with the diameter of 60mm, and a configuration with a thickness of 10mm, and faces each other from the place of 100mm from the direction core of a path of the obtained quartz-glass ingot, and the head. Moreover, Na of 3 and the test piece for K analysis were cut down 10x10x5mm from directly under [of the test piece logging section for transmissometries]. Permeability was measured with the spectrophotometer for ultraviolet. Moreover, the radio-activation analysis by thermal neutron line irradiation performed the fixed quantity of Na and K.

[0029] Moreover, the sample for the elemental analyses of alkaline earth metal, transition metals, and aluminum was started from the place contiguous to those test pieces. The fixed quantity of each element was performed by the inductive-coupling type plasma atomic emission spectroscopy. Consequently, Mg of the alkaline earth metal of the test piece of an example 1, calcium, and each element concentration of Sc, Ti, V, Cr, Mn, Fe, Co, nickel, Cu, and Zn of transition metals were 20 or less ppb, respectively. Moreover, the concentration of aluminum was 5ppb. Furthermore, Na concentration of the test piece of an example 1 was 2ppb, and K concentration was below a minimum limit of detection (50ppb).

[0030] As a result of evaluating a transparency property, the absorption coefficient with a wavelength [of the test piece of an example 1] of 193nm was set to 0.001cm-1, and when converted into the internal transmittance, the very good value of 99.9% per cm was acquired. In addition, the absorption coefficient was computed by the following formulas. Absorption coefficient = theoretical permeability is permeability it is decided by zero only by the reflection loss on the front face of a sample in -ln (permeability / theoretical permeability) / test piece thickness at this time that internal-resorption loss will be.

[0031] In addition, when the refractive-index homogeneity of the obtained quartz-glass ingot was measured by the Fizeau interferometer which used helium-Ne laser as the light source, it turns out in a phi200mm field that the maximum of a refractive-index difference is a very homogeneous thing called 1x10-6.

[0032]

[Example 2] By the same method as an example 1, it has arranged and the quartz glass of an example 2 compounded the distance to the laminating point from synthetic furnace refractories so that it might be set to 200mm by the shortest. By this method, the quartz-glass ingot with a diameter [of 200mm] and a length of 600mm was obtained. Optical polish was given to the 2nd page which cuts down the test piece for transmissometries with the diameter of 60mm, and a configuration with a thickness of 10mm, and faces each other from the place of 100mm from the direction core of a path of the obtained quartz-glass ingot, and the head. Moreover, Na of 3 and the test piece for K analysis were cut down 10x10x5mm from directly under [of the test piece logging section for transmissometries]. Moreover, the sample for the elemental analyses of alkaline earth metal, transition metals, and aluminum was started from the place contiguous to those test pieces.
[0033] Consequently, Mg of the alkaline earth metal of the test piece of an example 2, calcium, and each element concentration of Sc, Ti, V, Cr, Mn, Fe, Co, nickel, Cu, and Zn of transition metals were 20 or less ppb, respectively. Moreover, the concentration of aluminum was 25ppb. Furthermore Na concentration of the test piece of an example 2 was 19ppb, and K concentration was below a minimum limit of detection (50ppb). Moreover, the absorption coefficient with a wavelength of 193nm was set to 0.002cm-1, and the good value of [converting into an internal transmittance] 99.8% per cm was acquired.
[0034] Moreover, when the refractive-index homogeneity of the obtained quartz-glass ingot was measured, the maximum of a refractive-index difference was 2x10-6 in the phi150mm field.
[0035]
[The example 1 of comparison] In order to raise refractive-index homogeneity further about the ingot of an example 2, it heat-treated in argon atmosphere in pressure 10 kg/cm2, 1900 degrees-C [of retention temperatures], and holding-time 10 hours. The quartz-glass base material obtained in the example 2 to process was set to phi200mm made from carbon graphite, and the dies body with a thickness of 10mm. Moreover, in order to prevent that it becomes impossible to take out a matrix from a dies body after heat treatment, the carbon fiber felt was installed in the inside of a dies body. In addition, a processing furnace has a heater in the vertical section and a flank, and the whole heating furnace is covered by the thermal break. Thus, the sample with a thickness [of phi obtained 190] of 50mm was made into the example 2 of comparison. The test piece for transmissometries which has the diameter of 60mm and a configuration with a thickness of 10mm from the direction core of a path of the sample of this example 2 of comparison and the thickness direction core was cut down, and optical polish was given to the 2nd page which faces each other. Moreover, Na of 3 and the test piece for K analysis were cut down 10x10x5mm from directly under [of the test piece logging section for transmissometries]. Moreover, the sample for the elemental analyses of alkaline earth metal, transition metals, and aluminum was started from the place contiguous to those test pieces.
[0036] Consequently, Mg of the alkaline earth metal of the test piece of the example 2 of comparison, calcium, and each element concentration of Sc, Ti, V, Cr, Mn, Fe, Co, nickel, Cu, and Zn of transition metals were 20 or less ppb, respectively. Moreover, the concentration of aluminum was 10ppb. Furthermore, Na concentration of the test piece of the example 2 of comparison was 120ppb, and K concentration was below a minimum limit of detection (50ppb). Moreover, when the absorption coefficient with a wavelength of 193nm was very as large as 0.048cm-1 and was converted into the internal transmittance, it turns out [95.3% per cm, and] that it is poor.
[0037]
[The example 2 of comparison] The sample of the example 2 of comparison was produced like the method of the example 2 of comparison. However, the quartz-glass base material obtained in the example 2 was installed into the matrix of the bore of 150mm which fused and produced SiO2 powder or SiO2 powder, and the shape of a doughnut of 250mm of appearances, and heat-treated by installing it in the dies body made from carbon graphite with a bore of 300mm further. Thus, phi150mm and the sample with a thickness of 50mm were made into the example 3 of comparison. The test piece for evaluation was cut down from the core of the sample of this example 3 of comparison.
[0038] Mg of the alkaline earth metal of the test piece of the example 3 of comparison, calcium, and

each element concentration of Sc, Ti, V, Cr, Mn, Fe, Co, nickel, Cu, and Zn of transition metals were 20 or less ppb, respectively as a result of analysis. Moreover, the concentration of aluminum was 10ppb. Furthermore, Na concentration of the test piece of the example 3 of comparison was 47ppb, and K concentration was below a minimum limit of detection (50ppb). Moreover, the absorption coefficient with a wavelength of 193nm was 0.012cm-1, and when converted into the internal transmittance, it turns out [98.8% per cm, and] that it is poor.

[0039] Drawing which plotted Na concentration dependency of an absorption coefficient with a wavelength of 193nm was shown in drawing 2 about the test piece of examples 1 and 2 and the examples 1 and 2 of comparison. As shown in drawing 2 , it depended to Na concentration strongly, and when Na concentration was set to 20 or less ppb, as for absorption, zero found [the absorption coefficient with a wavelength of 193nm] the bird clapper mostly further.

[0040]

[The example 3 of comparison] Although the sample of the example 3 of comparison was fundamentally produced by the same method as an example 1, a different point was replaced with the quartz-glass board as a target, and the container which covered with SiC the inside and the undersurface of the refractories of the diameter of a cylinder made from the alumina was used for it. The bore of this container was phi300mm. This container was made to deposit direct quartz glass, and the sample of phi300mm and the example 3 of comparison with a thickness of 200mm was produced. The test piece for evaluation was cut down from the core of the sample of the acquired example 3 of comparison.

[0041] Mg of the alkaline earth metal of the test piece of the example 3 of comparison, calcium, and each element concentration of Sc, Ti, V, Cr, Mn, Fe, Co, nickel, Cu, and Zn of transition metals were 20 or less ppb, respectively as a result of analysis. Moreover, the concentration of aluminum was 10ppb. K concentration was 100ppb although Na concentration of the test piece of the example 4 of comparison was furthermore 13ppb. And the absorption coefficient with a wavelength [of this test piece] of 193nm was 0.010cm-1, and when converted into the internal transmittance, it turns out [99.0% per cm, and] that it is poor.

[0042]

[Example 3] 70mm in the maximum aperture of 250mm among the quartz-glass light faculty material of this invention, and thickness The maximum refractive-index difference in an excimer laser irradiation field is **n<=2x10-6. It migrates to the whole region. the rate of the maximum birefringence -- 2 or less nm/cm -- it is -- further -- a member -- Mg of alkaline earth metal, calcium, Sc, Ti, V, Cr of transition metals, Each element concentration of Mn, Fe, Co, nickel, Cu, and Zn, respectively 20 or less ppb, 5 - 100ppb and Na concentration of alkali metal produced [the concentration of aluminum] the ArF excimer laser stepper projection lens using the member in which 20 or less ppb and K high impurity concentration have the property of 50 or less ppb. And the resolution of the obtained projection optical system was able to attain 0.19 micrometers in the line and the space, and was able to obtain the image formation performance good as an ArF excimer laser stepper.

[0043]

[Effect of the Invention] According to this invention, are installed, for example in excimer laser lithography equipment etc. The throughput of the optical system of the laser of ultraviolet [250nm or less], vacuum ultraviolet radiation, or this wavelength field is raised. The quartz-glass optical member which can realize optical system which can carry out image formation to homogeneity over a large field, It became possible to offer the optical element which has a high throughput to laser of ultraviolet [250nm or less], vacuum ultraviolet radiation, or this wavelength field, such as a fiber, window part material, a mirror, an etalon, and prism. Furthermore, it became possible to offer the highly precise optical lithography equipment using the light source with a wavelength of 250nm or less.

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(57) [Subject of Invention]

Quartz glass optical member, its manufacturing method, and projection exposure equipment

(57) [Summary]

[Task] There are cases when the wavelength becomes the vacuum UV region of below wavelength 200 nm, the transmittance (of the optical member) would be degraded abruptly; because of this, the absorbance would become more than several % per 1 cm light path length so that it utterly cannot be used as optical member of ArF excimer laser stepper.

[Solving Means] In the quartz glass optical member to be used in the optical system of wavelength region below 250 nm, the concentration of the Na contained in the quartz glass is set to be below 20 ppb.

[Scope of the Patent Claim]

[Claim Item 1] A quartz glass optical member having the following characteristics: In the quartz glass optical member to be used in the optical system of wavelength region below 250 nm, the concentration of the Na contained in the quartz glass is below 20 ppb.

[Claim Item 2] A quartz glass optical member having the following characteristics: In the quartz glass optical member to be used in the optical system of wavelength region below 250 nm, the concentration of the Na contained in the quartz glass is below 50 ppb and the concentration of the Al is 5 to 100 ppb.

[Claim Item 3] In the quartz glass optical member described in Claim Item 1 or 2, the concentration of each element of the transition metals and the alkali metals and the alkaline earth metals is (each) below 20 ppb.

[Claim Item 4] A quartz glass optical member having the following characteristics: In the quartz glass optical member to be used in the optical system of wavelength region below 250 nm, the mol concentration ratio of the Na and Al contained in the quartz glass is: $[Na]/[Al] \leq 1$.

[Claim Item 5] A manufacturing method of quartz glass having the following characteristics: In a synthesis furnace, a high purity silicon compound sprayed from a burner is hydrolyzed in an oxyhydrogen flame to form fine silica particles and the particles are deposited onto a target to be consolidated into glass, the distance between the position where the aforementioned fine particles reaching the target and the synthesis furnace is set to be more than 250 mm.

[Claim Item 6] A manufacturing method of quartz glass having the following characteristics: In a synthesis furnace, a high purity silicon compound sprayed from a burner is hydrolyzed in an oxyhydrogen flame to form fine silica particles and the particles are deposited onto a target to be consolidate into glass, the refractory material forming the furnace wall of the synthesis furnace is a refractory composed of alumina as major component.

[Claim Item 7] It is an equipment for projection-exposing the pattern image of a mask onto a substrate by using a projection optical system; the projection-exposure equipment is composed of the illumination optical system for illuminating the mask using a light of wavelength below 250 nm as exposure light and the projection optical system which includes the quartz glass optical member described in any of the Claim Items 1 through 4 to form the aforementioned mask pattern onto a substrate.

[Claim Item 8] It is an equipment for projection-exposing the pattern image of a mask onto a substrate by using a projection optical system; the projection-exposure equipment is composed of the illumination optical system which includes the quartz glass optical member described in any of the Claim Items 1 through 4 to illuminate the mask using a light of wavelength region below 250 nm as exposure light and a projection optical system for forming the pattern image of the aforementioned mask onto a substrate.

[Detailed Explanation of the Invention]

[0001]

[The Technical Field Belonging to the Invention] The present invention is related to the synthetic quartz glass optical members to be used as lens member, fiber, window material, mirror, echelon, prism, etc. optical elements of the illumination optical system or image forming optical system using the UV below 250nm, vacuum UV or the same wavelength region laser as light source, for example, the excimer laser lithography equipment, light CVD equipment, laser process equipment, etc. and the photo-lithography equipment using this quartz glass optical member for a portion or the entire system of the optical system.

[0002]

[Conventional Technology] Hitherto, in the photo-lithography in that fine patterns of integrated circuits are exposure-transcribed onto a wafer of silicon, etc., a so called stepper, shrinkage projection type exposure equipment is being employed. The optical system of this stepper is constructed by an illumination optical system to homogeneously illuminate the light of the light source onto the reticle drawn with integrated circuit pattern and the projection optical system to shrink the integrated circuit pattern of the reticle (for example, 1/5) and projection-transcribe onto the wafer. The equipment for transcribing integrated circuit patterns onto a wafer by using this kind of light is called as photo-lithography in general term. The degree of resolution of the transcribed pattern onto the wafer is required to be higher accompanying the high integration of LSI in recent years. In this, since the degree of the resolution of the transcribed pattern would be proportional to the inverse number of the numerical aperture of the projection optical lens system and the wavelength of the light source, it is

possible to obtain higher resolution by raise the numerical aperture or by shortening the wavelength of the light source. However, there is a limit on the numerical aperture of the lens from the standpoint of manufacturing. Therefore, for raising the degree of resolution, shortening of the wavelength of the light source would become the only option. Because of this, the light source of stepper is advancing to a shorter wavelength from the g line (436 nm) to i line (365 nm) and further to KrF (248 nm) and ArF (193 nm) excimer lasers. Especially, for manufacturing the super LSI of DRAM possessing memory capacity of more than 64, 256 megabits or 1, 4 gigabits, the line & space (mark of the resolution degree of a stepper) has to be made less than 0.3 um. In this, as the light source of the stepper, the only option is to use UV of below 250 nm of excimer laser, etc. or vacuum UV.

[0003] Generally, the optical glass used in the lens members of the illumination optical system or the projection optical system of a stepper using a light source of wavelength longer than i line, the transmittance would be abruptly lowered in the wavelength region of shorter than i line; especially at wavelength region shorter then 250 nm, most of the optical glasses would not transmit this light. Because of this, for the material useable in the optical system of the stepper using excimer laser as light source, it is limited to quartz glasses and a portion of crystal materials. Among them, especially quartz glasses is high transmittance in wavelength region below 250 nm, thus it would be the material not only for the excimer laser stepper but also can be widely used in the optical system of general UV vacuum lights.

[0 004] However, in the case where quartz glass is used for the optical system of photo-lithography, for exposing a large area of integrated circuit pattern with high resolution, an extremely high quality would be demanded for the quartz glass optical member. For example, the refractive index distribution of the member is required to be in the order of 10^{-6} for an extremely large aperture of diameter 200 mm level. And reducing the double refraction amount, namely reducing the strain inside the optical member would be important against the degree of resolution of the optical system, similarly to enhancing the homogeneity of the refractive index distribution.

[0005] Furthermore, it is required simultaneously that the transmittance is extremely superior in addition to the good homogeneity related to the refractive index and the high quality in respect to strain. For example, in the projection optical system of photo-lithography, for the aberration correction, very many lenses having curvature would be required. Because of this, in some cases, the total light path length of the entire projection optical system could be more than 1000 mm. In this case, for maintaining the throughput of the projection optical system to be more than 80%, a high transmittance of so called internal transmittance more than 99.8% per 1cm of optical member (below 0.002 cm^{-1} if converted to internal absorbance) would be required. Furthermore, such high transmittance is not only required to be present in the center portion but also has to be maintained for the entire region. Because of this, among the simply called quartz glasses, those can be used for precision optical system such as excimer laser stepper are limited.

[0006] Quartz glasses can be roughly classified into fused quartz glass and synthetic quartz glass. Fused quartz glasses are obtained by electrical fusion or flame fusion of the natural crystallized quartz powders. Synthetic quartz glasses are further classified according to the manufacturing method. Synthetic quartz glasses can be obtained by the direct method, the soot method, the plasma method, etc. vapor phase synthesis methods.

[0007] First of all, the direct method is as follows: for the raw material, a high purity silicon compound (silicon tetrachloride, etc.) is used; the raw material is hydrolyzed by an oxyhydrogen flame to form quartz glass fine particles (soot); the particles are deposited onto a target being rotated and being pulled up and fused to be consolidated to transparency in one step; by this a quartz glass ingot is obtained. And for making the quartz glass optical member obtained by this method to a higher quality material, a method, in that after the primary process of the quartz glass synthesis, a secondary heat-treatment is performed to obtain the desired physical properties, has been tried. For example, by performing the secondary heat-treatment at around 2000 degree C, it is known that the homogeneity of the refractive index can be enhanced.

[0008] Next, the soot method is as follows: for the raw material a high purity silicon compound is used; the raw material is hydrolyzed by an oxyhydrogen flame to form soot; the soot is deposited onto a target to obtain a soot chunk (preform); after this, it is consolidated to transparent quartz glass ingot by a secondary treatment. And, the plasma method is as follows: for the raw material, a high purity silicon compound is used; the raw material is oxidized by the high

frequency plasma flame of oxygen + argon mixture to form soot; the soot is deposited onto a target being rotated and being pulled up and fused to be consolidated to transparency in one step; by this a quartz, glass ingot is obtained.

[0009]

[The Problem to be Solved by the Invention] The synthetic quartz glasses obtained by these manufacturing methods are generally fewer in metallic impurities (higher in purity) compared to the fused quartz glasses. Therefore, it is possible to obtain a large aperture and homogeneous quartz glass optical member which possesses a high transmittance at the UV light wavelength region of below 250 nm; it is considered to be hopeful that for the optical system of photo-lithography of excimer laser stepper, etc., the synthetic quartz glasses can be employed.

[0010] However, even in this kind of synthetic quartz glass, it has been difficult to secure more than 99.8% transmittance per 1 cm transmission light path of the member at the wavelength region of below 250 nm. Especially, if it is a vacuum UV region of below wavelength 250 nm, the transmittance would deteriorate; thus, it cannot be employed utterly as the optical member of the ArF excimer laser stepper: the absorption amount per 1 cm optical path length would become more than several %.

[0011] Furthermore, for example, in the case such as the projection optical system of photo-lithography where a high precision quartz glass is required, it would be necessary that the material possesses good transmitting ability and

simultaneously is high quality in refractive index homogeneity at extremely large aperture of diameter ca. 200 mm and in strain.

[0012]

[The Means Used to Solve the Problem] Then, the present inventors, first of all, investigated the effect of the metallic impurities against the UV transmitting ability of synthetic quartz glass. As a result, it was verified that even the synthetic quartz glass whose internal transmittance at 248 nm of the wavelength of KrF excimer laser is more than 99.9 % per light path length 1 cm, it was found through further investigation of the transmission property on the shorter wavelength that the transmittance would be lowered abruptly in the wavelength region of below 220 nm. The internal transmittance at 193 nm of the wavelength of ArF excimer laser is below 99 % per light path length 1 cm; thus it cannot be used as optical member.

[0013] The present inventors, carried out novel studies on the causes of the abrupt transmittance lowering of the synthetic quartz glass at the vacuum UV region of below wavelength 220 nm. As a result, it was found that the factor governing the transmittance of this region is the alkali metal impurities. In particular, Na affects the transmittance of this wavelength region greatly; however as shown in Fig 2, when the Na concentration become less than 20 ppb, essentially no absorption would occur.

[0014] Accordingly, the present invention provides a quartz glass optical member having the following characteristics: In the quartz glass optical member to be used in the optical system of wavelength region below 250 nm, the concentration of the

Na contained in the quartz glass is below 20 ppb. And the present inventors also discovered that as an additional important point, if the Al is contained in a suitable amount, even if the Na content increases up to the same amount of the Al in mol concentration, essentially no absorption would occur at the wavelength region of below 220 nm.

[0015] Accordingly, the present invention provides a quartz glass optical member having the following characteristics: In the quartz glass optical member to be used in the optical system of wavelength region below 250 nm, the mol concentration ratio of Na and Al is set to be: $[Na]/Al] \leq 1$.

[0016]

[Implementation Mode of the Invention] As described above, in the present invention, it was discovered that the abrupt transmittance lowering of quartz glass at the UV region of below wavelength 250 nm, especially the vacuum UV region of below wavelength 220 nm, is caused by alkali metals, especially Na. Na is present in the air, water and human body, etc. and it can easily diffuse; thus it is a material which can extremely easily contaminate the optical member. Further, under high temperature condition, diffuison of Na can easily occur. Because of this, when a quartz glass member is for example, heat-treated in an electric furnace to higher than several hundreds degree C, it would easily diffuse to the inside of the member; especially at temperature above 1,000 degree C, it could become the cause of devitrification.

[0017] The present inventors experimentally verified that for example, for achieving the high homogeneity required for the member of the projection optical

system of photo-lithography, if it is performed for a secondary heat-treatment at the vicinity of 2,000 degree C, Na would easily diffuse into the member. It became clear that no matter how the constructing materials of the heat-treatment furnace inside are made, for example, the insulating material and the test container made of normal carbon are made into high purity, especially no matter how the Na impurity is reduced, there would be a contamination of several tens ppb level inside the quartz glass member after the heat-treatment.

[0018] It became clear that K would not be occluded by the aforementioned secondary heat-treatment, even though K is one of the alkali metals. For example, even in the aforementioned heat-treatment at the vicinity of 2,000 degree C, the concentration of K can be achieved to be less than 50 ppb; it was verified that this level of K would not affect the transmittance of the wavelength below 200 nm. It is thought that this is due to that the diffusion coefficient of K inside the quartz glass is smaller than that of Na.

[0019] Accordingly, although K would affect the transmittance of the wavelength region of less than 220 nm, its effect is smaller compared to Na; when K is made to be below 50 ppb, it can be made that essentially no transmittance lowering at the wavelength below 220 nm would occur. Based on the aforementioned points, as a method of reducing the alkali metal impurities (especially Na) in the quartz glass, the present inventors adapted the method of achieving homogenization of the refractive index during the synthesis without performing the secondary heat-treatment. However, when simply the homogenization during the synthesis is achieved, it is unavoidable that there would be a danger that Na in small amount

would be contaminated into the finished quartz glass. For example, there is a possibility that the impurities can be released from the refractory material used as the synthesis furnace wall of quartz glass under high temperature. This refractory material is generally employed around the quartz glass ingot of the synthesis furnace inside as insulator. Here, the present inventors verified that it is possible to lower the contamination of Na concentration to be below 20 ppb, the concentration of Li, K to be below 50 ppb. In concrete term, by the arrangement of maintaining the distance from the refractory material inside surface of the synthesis furnace to the deposition layer point to be more than 250 mm, the present invention can be achieved. In this, the deposition point means the location where the soot sprayed from the burner would reach onto the ingot. Most of the soot would be captured by the ingot at this deposition point.

[0020] And, in the conventional synthesis furnace, the refractory material, the commercial firebricks as specified by JIS standard are being used. For example, clay type firebricks, silica firebricks, high alumina firebricks are available. For example, alumina firebricks are composed of about 90% Al_2O_3, as impurity, 0.5—1% of Na_2O (by X-ray fluorescence analysis) are contained. This Na_2O from the refractory would become the cause of Na diffusion into quartz glass.

[0021] Therefore, in the present invention, as the refractory of the synthesis furnace inside, refractory material with alumina as major component containing no Na_2O was employed. In concrete term, refractory material composed of more than 99% Al_2O_3 was prepared; and this was employed. When the synthesis furnace possessing this refractory was used to synthesize quartz glass ingots, the

Na content in the quartz glass became less than the detection limit by the radio-activation analysis (below 1 ppb).

[0022] From this ingot, the desired shape of optical member was cu out; the Na concentration of the synthetic quartz glass optical member obtained after annealing became less than 10 ppb. Further, when the refractory with alumina (Al2O3) as major component (more than 99%) was employed, at least more than several tens ppb of Al would be contaminated into the quartz being synthesized. Al is an impurity for quartz glass; however when a small amount of Al coexists with about the same level of Na, it became clear that Al would act to suppress the absorption occurring by the presence of the Na.

[0023] The reason for this is deduced that by the presence of Al in the quartz glass, Al would bridge the non-bridging oxygen occurring by the presence of Na inside the quartz glass (to eliminate the non-bridging). Namely, in the quartz glass containing minute amount of Na, if about the same level of Al is contained, the UV absorption can be eliminated to obtain a superior UV property. However, if the Al content is too large, for example more than 100 ppb, absorption and/or the structural defects of Al itself would become problem; thus the content of the Al is preferably 5 ppb to 100 ppb.

[0024]

[Implementation Example 1]

<Synthesis of Quartz Glass> Fig 1 is an outline diagram showing the synthesis furnace for manufacturing the synthetic quartz glass. The burner 2 is arranged to the top portion of the refractory 1 (the refractory will be described later) of the

furnace wall of the synthesis furnace so that the tip-end of the burner would be facing the target. To the furnace wall, a window for viewing (not shown in the figure) and exhaust pipe are provided. To the bottom portion of the synthesis furnace, the target 4 forming the ingot is arranged.

[0025] For the burner, a multi-tube structure kind made of quartz glass was employed. In this burner, oxygen gas and hydrogen gas are mixed and combusted. As raw material, high purity silicon tetrachloride purity more than 99.9%; metallic impurity: Fe concentration below 10 ppb, Ni and Cr concentration below 2 ppb, is diluted by the carrier gas (normally oxygen) and sprayed from the center tube of the burner at raw material flow rate 30 g/minute. By the hydrolysis of the raw material in the flame at the burner tip-end, quartz glass fine particles (soot) are generated. The particles are deposited onto a target of diameter 200 (unit was not given in the Japanese patent; probably mm) which is being rotated at 7 rpm, vibrated with 80 mm moving distance at 90 second cycle, and pulled down at 4 mm per hour speed; the deposited particles are fused (melted) together simultaneously to synthesize an ingot. During this, the top portion of the ingot is covered by the flame. The hydrogen flow rate sprayed from the burner was about 500 slm and the ratio of the oxygen gas flow amount and the hydrogen flow amount was set to be: $O2/H2 = 0.4$.

[0026] By rotating and vibrating the target plate at certain cycle, the temperature distribution on the synthesis surface of the ingot top portion can be made smaller; thus the refractive index homogeneity of the obtained quartz glass would be enhanced. Furthermore, the target plate is being pulled down so that the position

of the synthesis surface of the ingot top portion is constantly maintained at identical distance from the burner. As above, by the rotation at certain cycle, vibration and moving-down of the target during the synthesis, no stira would be formed in 3 directions; thus the double refraction accompanying the stria would be absent so that a quartz glass ingot of refractive index homogeneity below 2 x 10^{-6} can be obtained.

[0027] And in this synthesis furnace, the distance from the refractory constructing the synthesis furnace to the synthesis surface is set to be 300 mm minimum (shortest distance) to carry out the synthesis. The synthesis surface means the location where the soot sprayed from the burner is reaching onto the top portion of the ingot. And, the refractory of the synthesis furnace is arranged so that the inside surface shape surrounding the quartz glass ingot is 600 mm length x 800 mm width x 800 mm height; the refractory was made of alumina (Al2O3). This refractory was prepared by mixing bubble shape alumina hollow particles with high alumina type binder and sintered at 1500 degree C for 24 hours to remove the volatile. The refractory is composed of more than 99.5% of Al2O3 and the content of Na2O is below the detection limit by the X-ray fluorescence analysis (0.03%).

[0028] By this method, a quartz glass ingot of diameter 300 mm, length 600 mm was obtained. Test pieces for transmittance measurement possessing the shape of diameter 60 mm, thickness 10 mm were cut from the radius direction center portion and 100 mm from the head of the obtained quartz glass ingot and the two facing surfaces were optically ground-polished. And from the immediately

beneath the portion where the transmittance measurement test pieces (specimens) were cut out, sample pieces of 10 x 10 x 5 mm^3 for Na, K analyses were cut out. The transmittance was measured by an UV spectrophotometer; and Na and K determinations were carried out by radio-activation analysis based on neutron irradiation (neutron activation analysis).

[0029] And from the location neighboring these test pieces, samples for the analysis of alkaline earth metals, transition metals and Al were cut out. The quantitative determination of each element was performed by the inductively coupled plasma emission spectrometric methods. The results were that each elemental concentration of Mg, Ca of alkaline earth metals, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn of transition metals of the test piece of Implementation 1 was (each) below 20 ppb. And the Al concentration was 5 ppb. Further the Na concentration of the test specimen piece of Implementation Example 1 was 2 ppb; and the K concentration was below the detection limit (50 ppb).

[0030] Transmission property evaluation was performed. Extremely good result was obtained: the absorption coefficient at 193 nm of the test piece of Implementation 1 was 0.001 cm^{-1}; converting to internal transmittance this is 99.9% per 1 cm. Furthermore, the absorption coefficient was calculated by the equation below: absorption coefficient = -1n (transmittance/theoretical transmittance)/test piece thickness; here, the theoretical transmittance means the transmittance when the internal absorption loss is zero and it is determined by the reflection loss of the sample surface alone.

[0031] Further, the refractive index homogeneity of the obtained quartz glass ingot was measured by a Fizeau interferometer using He-Ne laser light source: it was verified to be extremely homogeneous that the inside the region of ϕ 200 mm, the maximum value of refractive index difference was 1×10^{-6}.

[0032]

[Implementation Example 2] The quartz glass of Implementation Example 2 was synthesized by the same method of Implementation Example 1 and the distance from the refractory constructing the synthesis furnace to the synthesis surface was arranged to be 300 mm minimum (shortest distance). By this method, a quartz glass ingot of diameter 200 mm, length 600 mm was obtained. Test sample pieces for transmittance measurement possessing the shape of diameter 60 mm, thickness 10 mm were cut from the radius direction center portion and 100 mm from the head of the obtained quartz glass ingot and the two facing surfaces were optically ground-polished. And from the immediately beneath the portion where the transmittance measurement test piece was cut out, test pieces for Na, K analyses of $10 \times 10 \times 5$ mm^3 were cut out. And from the location neighboring these test pieces, samples for the analysis of alkaline earth metals, transition metals and Al were cut out.

[0033] The results were that each elemental concentration of Mg, Ca of alkaline earth metals, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn of transition metals of the test piece of Implementation 2 was below 20 ppb. And the Al concentration was 25 ppb. Further the Na concentration of the test specimen piece of Implementation Example 2 was 19 ppb; and the K concentration was below the detection limit (50

ppb). And the absorption coefficient at 193 nm of the test piece of Implementation 2 became 0.002 cm^{-1}; converting to internal transmittance this is 99.8% per 1 cm—a good value was obtained.

[0034] And, the refractive index homogeneity of the obtained quartz glass ingot was measured: the maximum value of refractive index difference was 2×10^{-6} within the region of ϕ 150 mm.

[0035]

[Comparison Example 1] For improving the refractive index homogeneity of the ingot of Implementation Example 2, it was heat-treated in an argon atmosphere, under pressure 10 kg/cm2, at the temperature maintained at 1900 degree C for 1 hour. The obtained quartz glass preform of the heat treated Implementation 2 was set into a outside mold made of carbon graphite measuring 200 mm in diameter (ϕ) and 10 mm in thickness. And for preventing the difficulty of removing from the mold after the heat-treatment, a carbon fiber felt was place on the inside surface of outside-mold. Further, the treatment furnace was equipped with heaters to the top, bottom portions and the side portion and the entire heating furnace was covered by insulation layer. The obtained sample of 190, thickness 50 mm is assumed to be Comparison Example 2 (misprint of Comparison Example 1). Test sample pieces for transmittance measurement possessing the shape of diameter 60 mm, thickness 10 mm were cut from the radius direction center portion and the thickness direction center portion of this Comparison Example 2 (misprint of Comparison Example 1) and the two facing surfaces were optically ground-polished. And from the immediately beneath the portion where the

transmittance measurement test piece was cut out, samples for Na, K analyses of $10 \times 10 \times 5\ mm^3$ were cut out. And from the location neighboring these test pieces, samples for the elemental analysis of alkaline earth metals, transition metals and Al were cut out.

[0036] The results were that each elemental concentration of Mg, Ca of alkaline earth metals, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn of transition metals of the test piece of Comparison Example 2 (misprint of Comparison Example 1) was (each) below 20 ppb. And the Al concentration was 10 ppb. Further the Na concentration of the test specimen piece of Comparison Example 2 (misprint of Comparison Example 1) was 120 ppb; and the K concentration was below the detection limit (50 ppb). And the absorption coefficient at 193 nm was extremely large: 0.048 cm^{-1}; converting to internal transmittance this is 95.3% per 1 cm—a poor value was obtained.

[0037]

[Comparison Example 2] The sample of Comparison Example 2 was prepared similarly to Comparison Example 2 (misprint of 1 ?). However, the quartz glass preform obtained in Comparison Example 2 was placed in a donut shape perform mold of inside diameter 150 mm, outside shape 250 mm prepared by SiO2 powders or by fusing SiO2 powders; this was then placed into a outside mold made of carbon graphite of inside diameter 300 mm and then the heat-treatment was performed. As above, the obtained sample of 150 mm, thickness 50 mm sample was assumed to be Comparison Sample 3 (misprint of 2 ?). From the

center portion of this Comparison Sample 3 (misprint of 2 ?), test pieces were cut out for evaluation.

[0038] The analytical results were that each elemental concentration of Mg, Ca of alkaline earth metals, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, *Zn* of transition metals of the test piece of Comparison Example 3 (misprint of Comparison Example 2) was (each) below 20 ppb. And the Al concentration was 10 ppb. Further the Na concentration of the test specimen piece of Comparison Example 3 (misprint of Comparison Example 2) was 47 ppb; and the K concentration was below the detection limit (50 ppb). And the absorption coefficient at 193 nm was 0.12 cm^{-1}; converting to internal transmittance this is 98.8% per 1 cm—it is clear that this is poor.

[0039] Relative to the test pieces of Implementation Example 1, 2 and Comparison Example 1, 2, the Na concentration dependencies of the absorption coefficient at wavelength 193 nm were plotted and shown in Fig 2. As shown in Fig 2, the absorption coefficient is strongly dependent on Na concentration; it is clear that when the Na concentration becomes less than 20 ppb, the absorption would become roughly zero.

[0040]

[Comparison Example 3] The samples of Comparison Example 3 were prepared by the method basically similarly to Implementation Example 1; the different point is that as the target, instead of a quartz glass plate, a container of cylindrical diameter prepared by alumina with the inside surface and the bottom surface lined with SiC was employed. The inside diameter (ϕ) was 300 mm. Into this

container, the quartz glass was directly deposited to prepare the sample of Comparison Example 3 measuring 300 mm in diameter and 200 mm in thickness. From the center portion of the obtained sample of Comparison Example 3, evaluation test pieces were cut out.

[0041] The analytical results were that each elemental concentration of Mg, Ca of alkaline earth metals, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn of transition metals of the test piece of Comparison Example 3 was (each) below 20 ppb. And the Al concentration was 10 ppb. Further the Na concentration of the test piece of Comparison Example 4 (misprint of Comparison Example 3) was 13 ppb; and the K concentration was 100 ppb. And the absorption coefficient of this test piece at 193 nm was 0.010cm^{-1}; converting to internal transmittance this is 99.0% per 1 cm—it is clear that this is poor.

[0042]

[Implementation Example 3] Among the quartz glass members of the present invention, the member possesses the properties below was used to prepare an ArF excimer laser stepper projection lens: the dimension was maximum aperture 250 mm, thickness 70 mm; the maximum refractive index difference (Δn) in the region of excimer laser irradiation: $\Delta n \leq 2 \times 10^{-6}$; the maximum double refractive index was below 2nm/cm; and for the entire region of the member, each elemental concentration of Mg, Ca of alkaline earth metals, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn below 20 ppb, the Al concentration was (each) 5—100 ppb and the Na concentration was below 20 ppb; and the K concentration was below 50 ppb. The obtained resolution degree of the projection optical system achieved the line &

space of 0.19 um; namely, a good image forming ability as ArF excimer laser stepper was obtained.

[0043]

[Effect of the Invention] Based on the present invention, quartz glass optical members which can be used to realize the optical system to be arranged in for, example, an excimer laser lithography equipment to enhance the throughput of the optical system of the UV light of below 250 nm, the vacuum UV or the same wavelength region laser to obtain homogeneous image forming over a wide region can be provided. It can also provide the fiber, window material, mirror, echelon, prism, etc. optical elements possessing high throughput against the UV below 250nm, vacuum UV or the same wavelength region laser. Furthermore, it can provide a high precision photo-lithography equipment using a light source of wavelength below 250 nm.

[Brief Explanation of Figures]

Fig 1 is an outline diagram showing the synthesis furnace for manufacturing the synthetic quartz glass.

Fig 2 is a diagram showing the relationship between the absorption coefficient of wavelength 193 nm of ArF excimer and the Na concentration of the synthetic quartz glass. The ordinate axis cm^-1 = cm^{-1}.

Fig. 1

QUARTZ GLASS SYNTHESIS EQUIPMENT

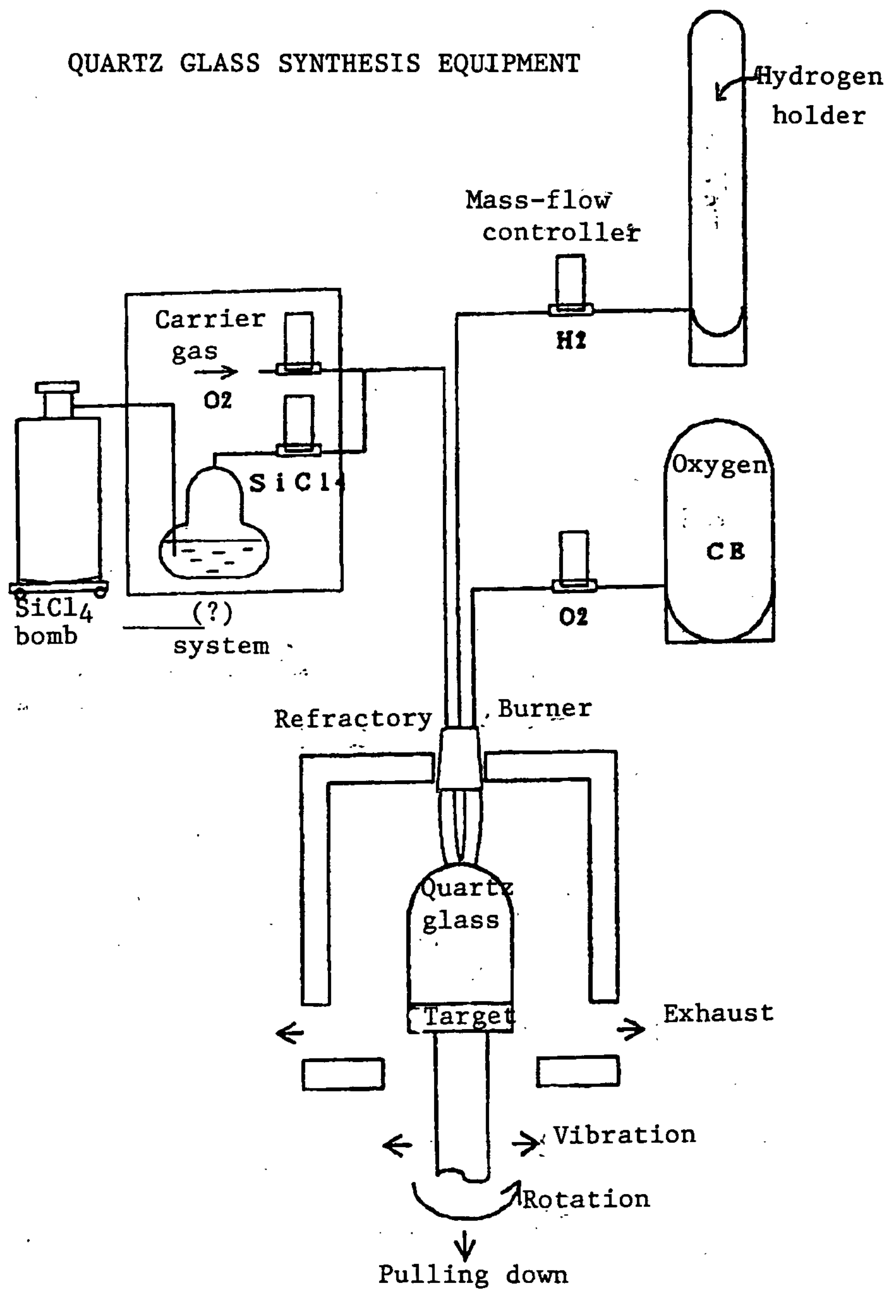
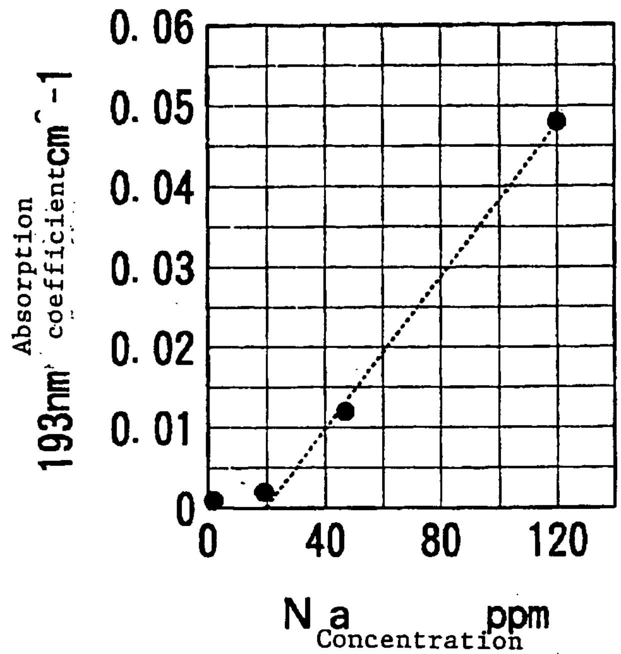


Fig 2


0.06
0.05
0.04
0.03
0.02
0.01
0
193nm Absorption coefficient cm^-1
0
40
80
120
Na Concentration ppm